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A NEW METHOD FOR THE PREPARATION OF α-KETO CARBOXYLIC ESTERS BY THE PHOTO-OXIDATION OF 1-(1-ETHOXYCARBONYLALKYL)PYRIDINIUM IODIDES

Takeshi TAKEDA* and Teruaki MUKAIYAMA**

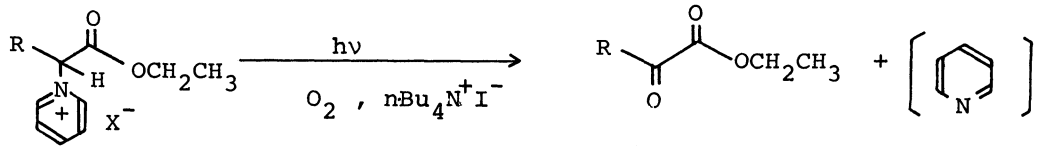
* Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

** Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113

α-Keto carboxylic esters were obtained in good yields by the photo-oxidation of 1-(1-ethoxycarbonylalkyl)pyridinium iodides in the presence of tetra-n-butylammonium iodide. Similarly, 1-methyl-2-(1-ethoxycarbonylalkylthio)pyridinium iodides were oxidized to give α-keto carboxylic esters.

In the previous paper$^{1)}$, it was shown that a variety of 1-(2-oxoalkyl)pyridinium iodides were oxidized with oxygen gas under irradiation with a high pressure mercury lamp to produce α-diketones in good yields. This result suggests that the direct oxidation of pyridinium salts or the other onium salts to carbonyl compounds may have a synthetic significance.

In the present investigation, it was established that α-keto carboxylic esters were obtained in fairly good yields by the photochemical reaction of 1-(1-ethoxycarbonylalkyl)pyridinium iodides with oxygen gas in the presence of tetra-n-butylammonium iodide.

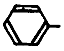
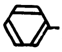
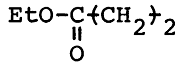


(I) X=I, Br (II)

For example, a solution of 1-(1-ethoxycarbonylundecyl)pyridinium iodide (1 mmol) and tetra-n-butylammonium iodide (0.73 mmol) in CH_3CN (20 ml) in a pyrex glass testtube was irradiated with a high pressure mercury lamp while oxygen was bubbled through. After the irradiation (60 min), the reaction mixture was poured into an aqueous Na_2SO_3 solution, and the mixture was shaken until a red color of iodine disappeared. An organic layer was extracted with ether and the extract was condensed under reduced pressure. The residue was chromatographed on silica gel and ethyl 2-oxododecanoate was isolated in 83% yield.

The present procedure was also successfully applied to the oxidation of pyridinium salts of α-bromocarboxylic esters when it was treated in the presence of 1.73 molar equivalent of tetra-n-butylammonium iodide. These results are listed in Table (I).

Table (I). The photo-oxidation of 1-(1-ethoxycarbonylalkyl)pyridinium iodides.

R	X	Time (min)	Yield (%)
	I	30	86
	Br	30	93
 CH_2-	I	60	27
$CH_3(CH_2)_9$	I	60	83
	Br	30	60
$CH_3(CH_2)_6$	I	60	75
$(CH_3)_2CHCH_2$-	I	60	63
 $EtO\text{-}\underset{\underset{O}{\Vert}}{C}(CH_2)_2$	I	60	16

In a similar manner, 1-methyl-2-(1-ethoxycarbonylalkylthio)pyridinium iodides were oxidized in the presence of 3.7 molar equivalent of tetra-n-butylammonium iodide to give the corresponding α-keto carboxylic esters in fairly good yields (see Table (II)). In these cases, the formation of a small amount of unidentified by-products was observed.

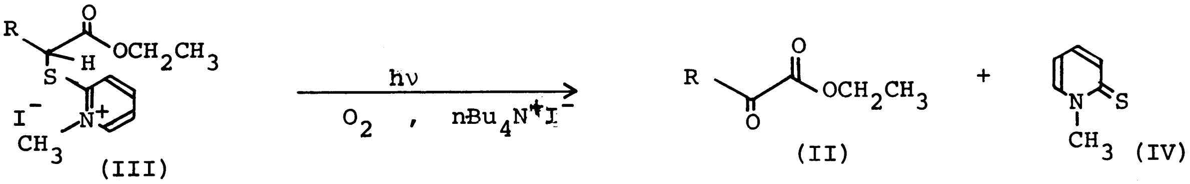
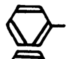
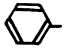


Table (II) The photo-oxidation of 1-methyl-2-(1-ethoxycarbonylalkylthio)-pyridinium iodides.

R	Time (min)	Yield (%) (II)	Yield (%) (IV)
	30	85	77
 CH_2-	60	35	59
$CH_3(CH_2)_9$	60	58	64
$CH_3(CH_2)_6$	60	61	66
$(CH_3)_2CHCH_2$-	60	57	56

Concerning the preparation of α-keto carboxylic esters by the oxidation of carboxylic esters, the direct oxidation with selenium oxide$^{2)}$ and through α-hydroxyimino carboxylic esters by employing ethyl nitrite$^{3)}$ were reported. The oxidation of α-halocarboxylic esters with dimethyl sulfoxide$^{4)}$ was also reported.

It is noted that the present method for the preparation of α-keto carboxylic esters by photo-oxidation of 1-(1-ethoxycarbonylalkyl)pyridinium iodides has some advantages over the above mentioned methods in the following point ; namely, the oxidation proceeds under mild reaction conditions by simply passing gaseous oxygen.

Further works on the scope and utility of the reaction are now in progress.

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